

Spark Plasma and Rate Controlled Sintering of High-Melting Point Nanocomposites

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Over the last decade, nano-structured materials, including nanocrystalline monolithic aggregates and nano-composites, became the object of increasing interest. To consolidate the nanocomposites and achieve desired properties the new technological processes have been applied. Rate Controlled Sintering and Spark Plasma Sintering are successfully used to obtain near fully dense high melting nanocomposites with grain size within nanometric scale and make sintering process faster and cheaper.

Keywords: RCS, SPS, TiN, Si₃N₄, Nanocomposites.

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1. INTRODUCTION

Nanostructured materials based on high melting compounds have been in the focus of research activity for many years. In particular, nanosized high melting point nitrides powders of different origins have been used in pressureless and spark plasma sintering. Properties of TiN (like the other high melting point materials) such as strength, hardness, fracture toughness, are very sensitive with respect to reduction of the grain size. Nanograined ceramics are expected lead to the improvement of these properties compared to conventional coarse-grained ceramics. For this

reason, the aim of our work is to investigate the densification kinetics, features of microstructure and properties for high melting point nanocomposite powders like nanocomposites TiN-Si₃N₄. In these compositions, the titanium nitride was a phase, which increased hardness, while Si₃N₄ increased the fracture toughness.

2. METHODS AND MATERIALS

Nanocrystalline powders of TiN produced by H C Starck GmbH (PVD) and silicon nitride prepared by plasmachemical synthesis (PCT ltd. Latvia) were used in the present investigation, see Table 1.

Table 1 – Properties of nanosized powders

Powder	Crystallite size, [nm]	Lattice parameter, [Å]	[O], wt.%	[N], wt.%
TiN	15	4,241 ± 0,001	1,8	19,8
β-Si ₃ N ₄	30-50	-	2,1	-

Powders TiN and β-Si₃N₄ were preliminary coated by surfactant – alkylsuccinimid (CUM) to preserve it from oxidation during storage.

To purify in particular all the nano-sized powders from CUM and oxygen (adsorbed or chemically bonded), the thermal treatment was carried out at high temperature under extra-dry hydrogen and nitrogen.

X-ray diffractometer (XRD – 7 with Cu K α radiation, Seifert-FPM, Freiberg, Germany) was used for the qualitative phase analysis. Particle size distribution of the nanopowders was estimated using light scattering particle size analyzer (Zetasizer 1000 HS, Malvern Instruments, United Kingdom) and TEM microscope (JEOL JEM-2100F, Japan). Vickers hardness and fracture toughness of sintered composites were measured at 50 g and 2 kg load conditions by MMT-3 (Buehler, USA) hardness tester. Nanohardness of consolidated nanomaterials was measured by a “Micron-Gamma” (National Aviation University, Ukraine) nanohardness tester using Berkovich indenter under 10 g and 20 g load conditions. Microstructure of the polished surface of sintered composites was examined by Field Emission Scanning Electron Microscope (NVision 40, Carl Zeiss SMT AG, Germany). Density of the consolidated nano-

composites was measured by Archimedes method in deionised water at room temperature. Crystallite size and lattice parameters have been estimated by XRD, specific surface areas of all the powders measured by means of nitrogen absorption (BET). Oxygen and nitrogen contents were determined by chemical analysis.

3. NANOCOMPOSITES CONSOLIDATION

3.1 Rate-Controlled Sintering (RCS)

We selected RCS because of its structurally oriented strategy [1, 2]. The advantage of the RCS over the linear heating rate regime with isothermal hold of standard sintering is the possibility to achieve a material's density of approximately 99.9 % while keeping the grain size bellow 100 nm.

The microstructure investigation, phase analyses and mechanical testing of TiN-based ceramic composites sintered under rate controlled regimes in vacuum dilatometer (10⁻⁵ torr) and gas pressure furnace have been carried out. Sintering of tested samples have been processed through the following manipulations. As-received powders of nanocompositions TiN-50wt. % Si₃N₄ were thermo-chemically treated in hydrogen (600 °C,

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60 °C/h). After thorough purification, the specimens were sintered under linear heating rate regimes without isothermal hold. Obtained dilatometric data for the specimens consolidation has been recalculated in rate-controlled schedule of sintering (see Fig. 1).

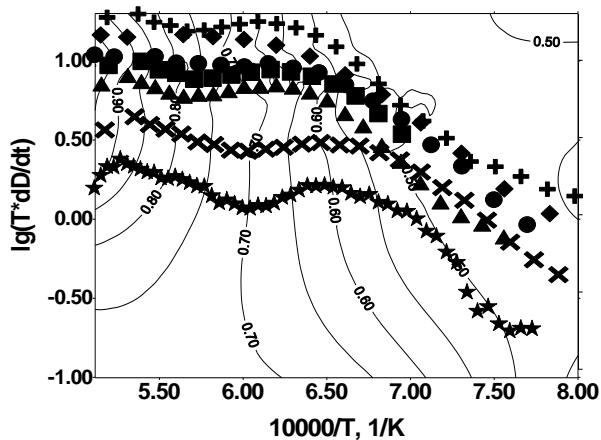


Fig. 1 – Kinetic field of response for TiN - Si₃N₄

Sintering of composition TiN – Si₃N₄ was accomplished in the regime of RCS using the cutting tool prototypes of 14 × 14 × 4 mm. All the specimens were preliminary thermally treated in hydrogen.

For this composition, the best sintering rate-controlled schedule has provided the RCS heating until the residual porosity achieved 8 – 9 %, then temperature drop of 50 °C and the final sintering stage of isothermal hold until full densification. Final stage was completely isothermal for 10 min. to allow the uniform porous structure to relax self similarly to zero. As it has been mentioned, all the TiN – Si₃N₄ composites were doped with 6 wt.% Y₂O₃ and 4 wt.% Al₂O₃ to form liquid phase with silica on grain boundaries at $T_{evt} = 1550$ °C. Sintering of the composite in hydrogen resulted in almost dense nanograined ceramics with the residual porosity of 1 % already at 1550 °C, whereas sintering in nitrogen demands much higher temperatures for completion of the densification. This fact can be explained by activation of powder surface in hydrogen, and *vice versa* passivation in nitrogen.

Additionally, the structural analysis of sintered specimens was carried out under (Fig. 2), to specify thoroughly grain size and pore size distribution. Fig. 2 demonstrates the microstructures of sintered in hydrogen composite 50 wt.% TiN – 50 wt.% Si₃N₄. Grain size distribution and porosity remains unchanged across the sample, and this fact is the best evidence of successful implementation of the sintering technique with shrinkage rate-controlled.

Large quantity of alumina-yttria-doped silicon nitride promotes full densification of this composite ceramics as well as retardation of grain growth during sintering in hydrogen or nitrogen at temperatures of 1550 – 1650 °C.

3.2 Spark Plasma Sintering (SPS)

Commonly, spark plasma sintering recognized by the most investigators as a FAST technique which gives the possibility to consolidate the desired materials in the

shortest time [3-5]. Short time of the process makes SPS attractive to consolidate nanopowders of various

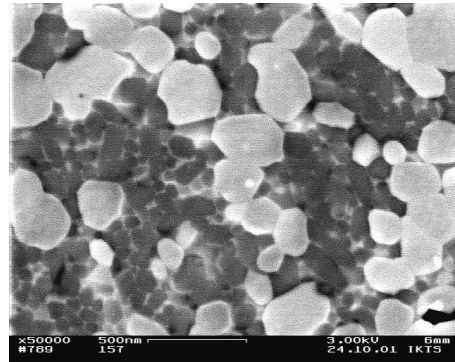


Fig. 2 – SEM images of sintered composition TiN – 50 wt.% Si₃N₄ in hydrogen

metals and ceramics and obtain nanostructured materials. Rapid heating rates around 100 – 200 °C/min with simultaneous increasing of pressure to 100 – 200 MPa with holding time at the maximal temperature 1 – 3 min, as usually used in SPS, caused to materials densities 95 – 97 % at the temperatures on the 150 – 200 °C lower than conventional sintering. But the structure of nanopowders sintered in this FAST schedules is around 250 – 400 nm [3, 4].

The SPS experiments have been carried out using an SPS- apparatus manufactured by FCT Systems GmbH ($T_{max} = 2400$ °C, $P_{max} = 250$ kN, $I_{max} = 8000$ A, $U_{max} = 10$ V, mediums: vacuum – $5 \cdot 10^{-2}$ mbar, nitrogen). All parameters were monitored during the experiment. Data about shrinkage of nanopowders during SPS consolidation process were monitored as travel of upper piston (the bottom piston is fixed) and recalculated in corresponded densities of specimens. Around 15 g of the nanopowder was loaded in a graphite die 30 mm diameter with punch unit and applying pressure 50 MPa to establish good contacts as between particles and graphite instruments – nanopowder. The sintering experiments were organized by the next schedule: nanopowder has been SPS consolidated in the one stage regime $P = 50$ MPa, heating rate 200 °C/min, $T = 1600$ °C without isothermal hold. And in few stage regime with sequential increasing of pressure from 50 to 70 MPa and decreasing of heating rate from 100 °C/min to 20 °C/min (Fig. 3). Ex hypothesi, increasing of the pressure will stimulate particle accommodation process during the sintering and provide the good contact between graphite punches and pellet. Decreasing of heating rate on the final stages of sintering will help to form the strong grain boundaries. Together these 2 factors intensify the densification process and decreasing of sintering temperature.

The electric current was pulsed periodically: pulse rate 20 ms and 1 ms pause between pulses. The temperature was measured by means of a pyrometer on the inner surface of the upper graphite piston. No isothermal hold at the high temperatures used to exclude uncontrolled grain growth. Experiments have been carried out in nitrogen.

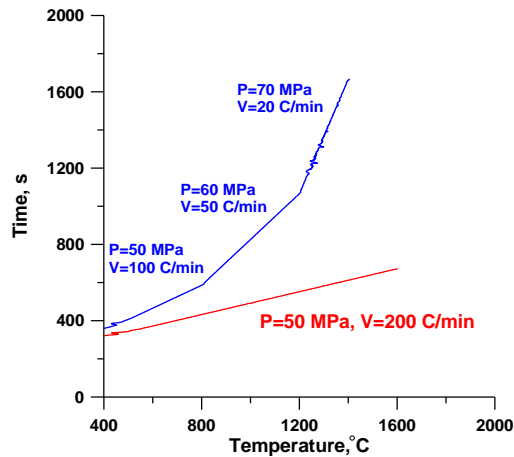


Fig. 3 – SPS regimes of TiCN nanopowder consolidation

Several preliminary runs had been carried out to estimate densification rates, define process control temperatures and built multiple step SPS regimes. Consolidation of composition TiN – 50 wt% Si₃N₄ doped by yttria and alumina has defined by the quantity of liquid phase formed at the temperatures 1400 – 1550 °C. Formation of liquid phase starts at the temperature around 1400 °C and promote densification process up to the peak temperature 1600 °C. Usually, consolidation of the same composites with a high content of silicon nitride phase carry out at the temperatures as high as 1650 °C. Applying non-linear SPS process we control the quantity of liquid phase on the final stage of sintering via regulation of heating rate and additionally stimulate the densification by increasing of external pressure. Finally, composition TiN-50 wt% Si₃N₄ could be fully densified (99 % of theoretical density) at the temperature 1550 °C to homogeneous nanocomposite. Estimated grains size of components for composition TiN-50 wt% Si₃N₄ are: around 50 nm for grains of silicon nitride and 100 – 200 nm for TiN (Fig. 4).

As discussed above, optimal peak temperature for titanium nitride to obtain dense ceramics with grains size around 50 nm is 1200 °C. For composition with silicon nitride the temperature 1550 °C is compromise between processes of composition densification and controlled grain growth of TiN nanoparticles in agglomerates.

Table 2 – Mechanical Properties of nanocomposite TiN – 50wt.% Si₃N₄ consolidated by SPS and RCS

Regime	Relative density (%)	Grain size, nm	Nanohardness, GPa	HV, GPa	k_{Ic} , MPa m ^{1/2}
RCS	99	~70	24±0.9	19,8 ±0,8	5,39
SPS	99	~100	22±1.3	19.5±1.9	5.5

SPS consolidated TiN-50 wt% Si₃N₄ composition showed relatively low nanohardness (~ 22 GPa) compared with RCS one, but good fracture toughness 5.5 MPa·m^{1/2}. It could be addressed to bigger volume of sintered sample. For SPS consolidated composition, the main role plays the volume of treated matter, conductivity of composition and preasure-heating rate characteristics. At the same time for RCS we operate only by heating rate parameter.

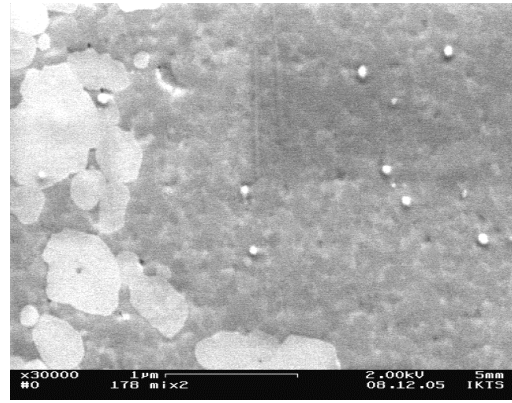


Fig. 4 – Scanning electron microscope micrograph of TiN-50% Si₃N₄ nanocomposition after few steps schedule SPS consolidation at 1550 °C in nitrogen

4. PROPERTIES OF NANOCOMPOSITES

It is generally accepted the characterization of the nanostructured materials by those methods, which allow showing up the relations between microstructure and properties of the material. Microhardness is one of easily accessible and structure sensitive. We characterized the composites in different scales: microscale (micro- and nanohardness) and macroscale (macrohardness and fracture toughness). The consolidated materials were almost fully densified, so their mechanical properties were closely related to their microstructures (Table 2). Hardness of nanomaterials is strongly depends on the grain size and grain boundary width. On the micrometer scale, this improvement may not be significant. However, the reduction of grain size by a factor of two in the nanoscale region (e.g., from 100 nm to 50 nm, or from 30 nm to 15 nm) leads to a substantial increase of the absolute number of grain boundaries per volume, which affects the grain boundary-dependent properties.

Mechanical properties of nanocomposites are presented in Table 2. In these compositions, the titanium nitride was a phase, which increased hardness, while the dopant (Si₃N₄) increased the fracture toughness.

5. CONCLUSIONS

Presented results proved the advantages of rate-controlled sintering technique as compared with conventional sintering mode like constant rate of heating. Optimal non-linear temperature-time path results in obtaining the dense, fine-grained and hard titanium nitride – silicon nitride nanocomposites from thermally treated nanocrystalline powders. This total

effect became possible due to remaining the structure uniform and nanograined.

Implementation of the few step spark plasma sintering schedule is potentially interesting to obtain dense nanocrystalline materials and consolidate different materials in a shortest time.

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